

Translation of Japanese Patent 6-116557

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(54) [Title of the invention]

Photostabilizer for cyanin pigments, and optical  
recording media containing said photostabilizer.

(57) [Abstract]

[Constitution] Photostabilizers for cyanin pigments comprising a phenol compound having in the same molecule 3 or 4 structural units represented by General Formula (1)



(in the formula  $R_1-R_3$  indicate a hydrogen atom or alkyl group), and optical recording media containing them.

[Benefits] They are highly safe and easy to handle, and are photostabilizers which have a very excellent photostabilizing effect on cyanin dyes, and enable optical recording media to be offered which have outstanding resistance to light.

[Claims]

[Claim 1] Photostabilizer for cyanin pigments comprising a phenol compound having in the same molecule 3 or 4 structural units represented by General Formula (1) ([Formula 1])

[Formula 1]



(in the formula R<sub>1</sub>-R<sub>3</sub>, indicate a hydrogen atom or alkyl group).

[Claim 2] Optical recording medium which contains a photostabilizer for cyanin pigments shown in Claim 1.

[Detailed explanation of the invention]

[0001]

[Field of industrial application] The present invention relates to photostabilizers for cyanin pigments and optical recording media containing them.

[0002]

[Prior art] Optical recording media include optical disks in which a thin film of cyan dye is used as a recording layer. The cyan dyes used here have poor photostability on their own, and it is necessary to employ an added photostabilizer.

[0003] Method using as photostabilizers metal complexes such as nickel compounds having thio ligands have been disclosed in Japanese Unexamined Patent 59-219852, Japanese Unexamined Patent 62-193891, Japanese

Unexamined Patent 62-207688, Japanese Unexamined Patent 63-19293 and Japanese Unexamined Patent 63-199248. These methods employ the mechanism of inactivating highly reactive singlet oxygen produced by light and returning it to triplet oxygen; however, they have the problem that decomposition of cyan pigments proceeds to a marked extent on long-term exposure to light.

[0004] As other photostabilizing compounds, methods using nitroso compounds have been disclosed in Japanese Unexamined Patent 2-300287, Japanese Unexamined Patent 2-300288 and Japanese Unexamined Patent 2-300289. However, most of these nitroso compounds have the problem that they have an undesirable nature, such as the fact that they are intensely toxic in themselves or their products of photodecomposition, etc., are intensely toxic so that the employment of nitroso compounds requires measures to ensure human safety, etc.

[0005] Moreover, a method using as photostabilizers compounds having a free trinitrophenylhydrazyl group is disclosed in Japanese Unexamined Patent 2-304055. However, compounds having free trinitrophenylhydrazyl groups are explosive, and handling them is very problematic.

[0006]

[Problem which the invention is intended to solve]  
The purpose of the present invention is to offer photostabilizers which solve these problems: namely, photostabilizers which raise the photostability of cyanin pigments and are easy to handle and highly safe.

Another purpose of the present invention is to offer optical recording media containing said photo-stabilizers.

[0007]

[Means for solving the problem] The present inventors have arrived at the present invention as the result of concerted investigations to solve the problems above, with the discovery that phenol compounds having in the same molecule 3 or 4 structural units represented by General Formula (1) ([Formula 2])

[0008]

[Formula 2]



[0009] (in the formula, R<sub>1</sub>-R<sub>3</sub> indicate a hydrogen atom or alkyl group) very considerably raise the photostability of cyanin dyes, and are also by nature easy to handle and highly safe, and that when said photostabilizers were used in optical recording media they were highly effective. Thus, the present invention is photostabilizers for cyanin pigments comprising a phenol compound having in the same molecule 3 or 4 structural units represented by General Formula (1) ([Formula 3])

[0010]

[Formula 3]

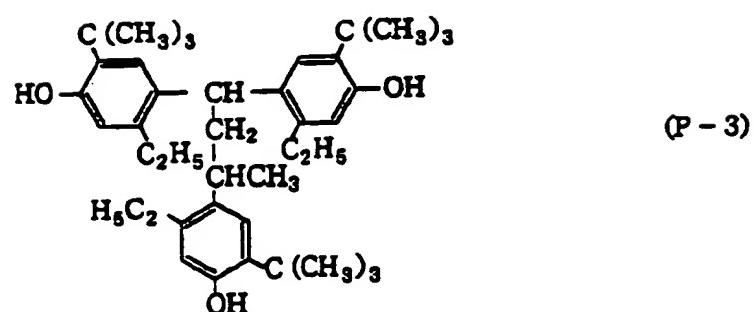
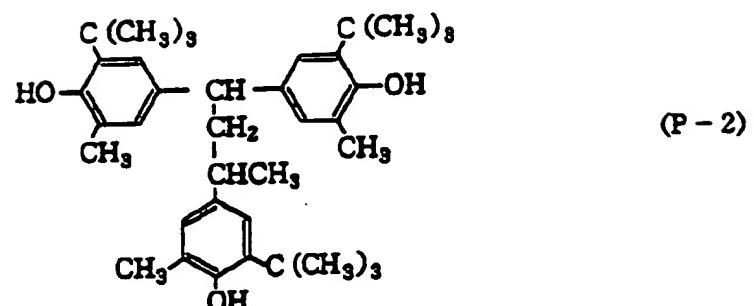
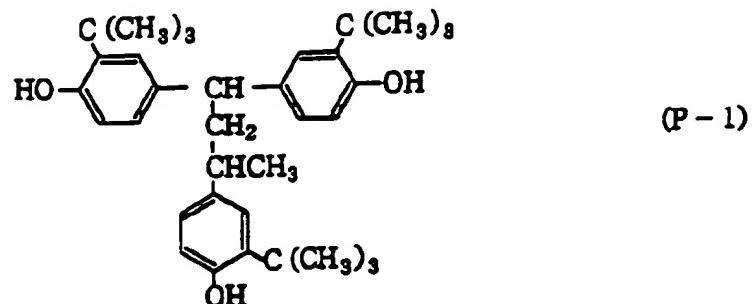


[0011] (in the formula R<sub>1</sub>-R<sub>3</sub> indicate a hydrogen atom or alkyl group.)

[0012] The present invention is discussed in detail below. Concrete examples of R<sub>1</sub>-R<sub>3</sub> in General Formula (1) of the present invention ([Formula 3]) include a hydrogen atom, and alkyl groups such as a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, t-butyl group, n-pentyl group, 2-methylbutyl group, n-hexyl group and n-octyl group, etc. Concrete examples of phenolic compounds having 3 or 4 structural units shown by General Formula (1) ([Formula 3]) are shown below (P-1 to P-21) ([Formula 4] to [Formula 10]).

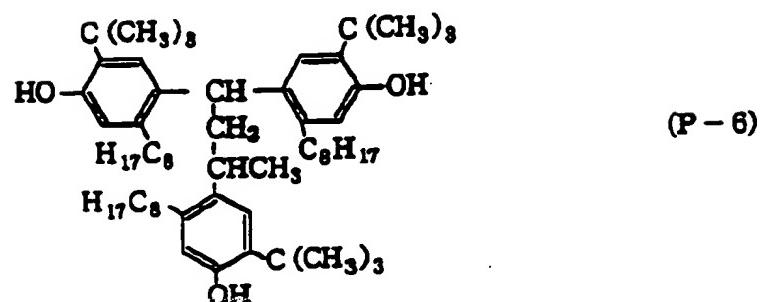
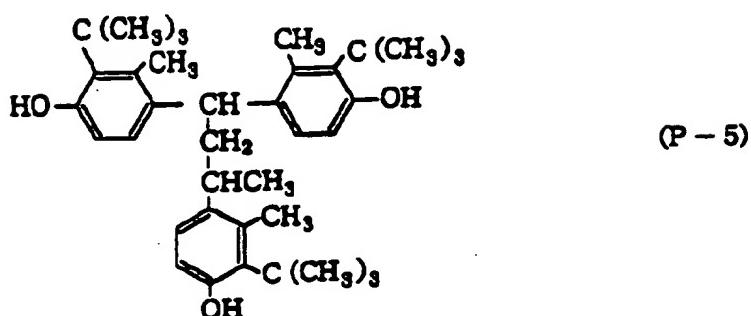
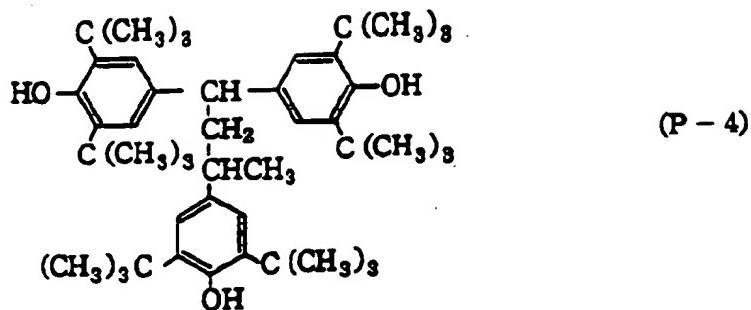
[0013]

[Formula 4]



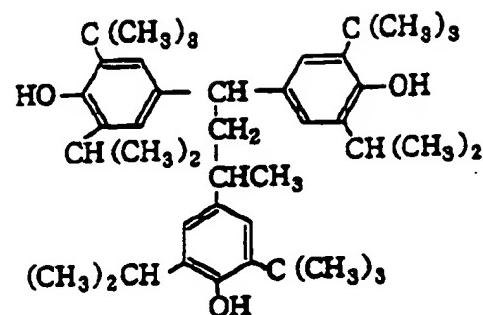
[0014]

[Formula 5]

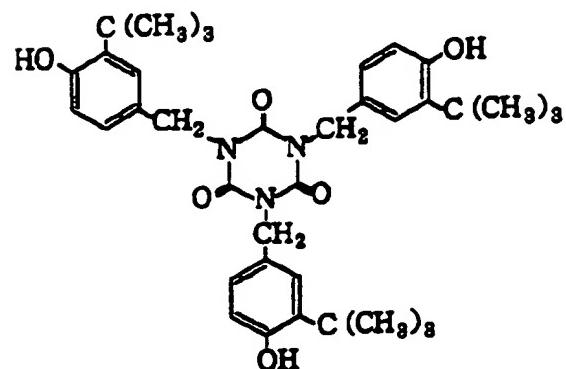


[0015]

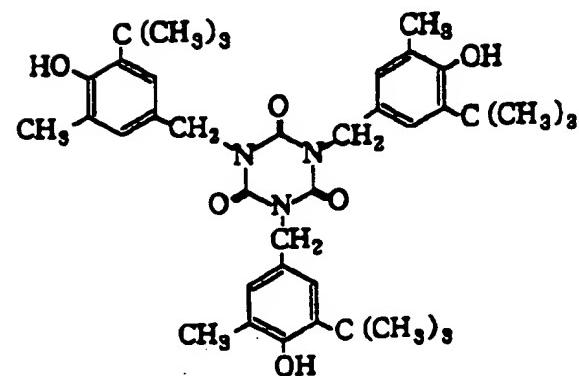
[Formula 6]



(P - 7)



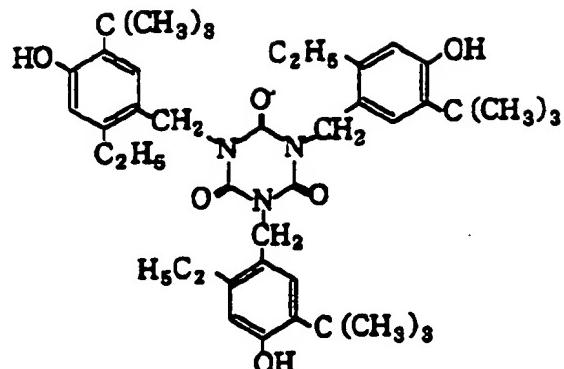
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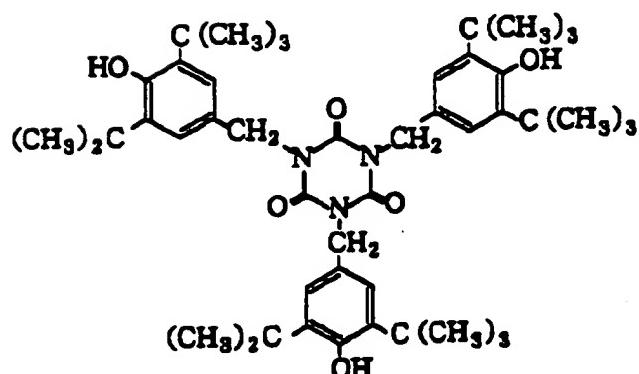
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[0016]

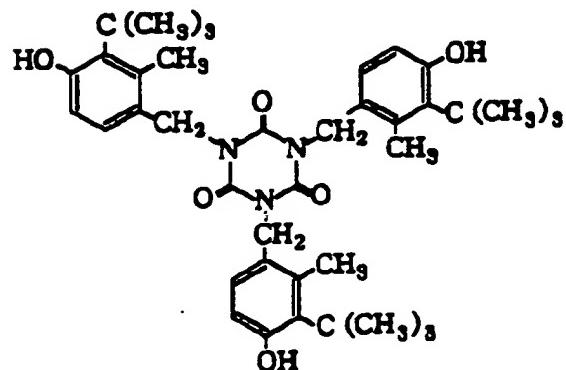
[Formula 7]



(P - 10)



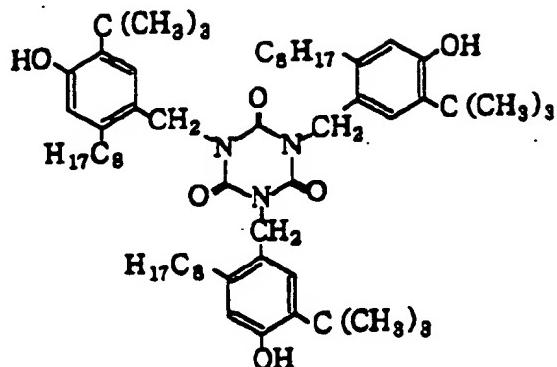
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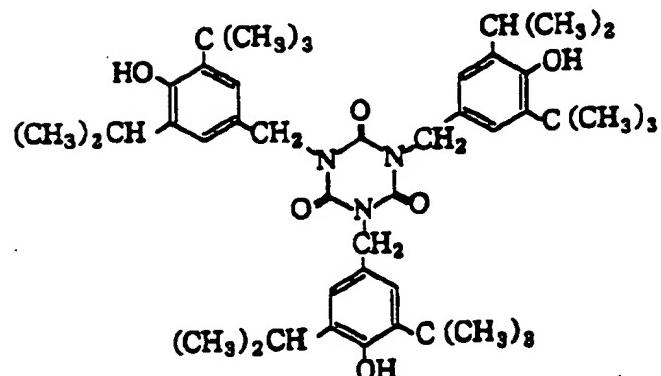
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[0017]

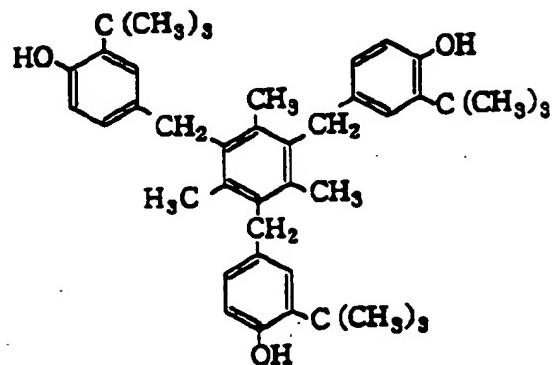
[Formula 8]



(P - 13)



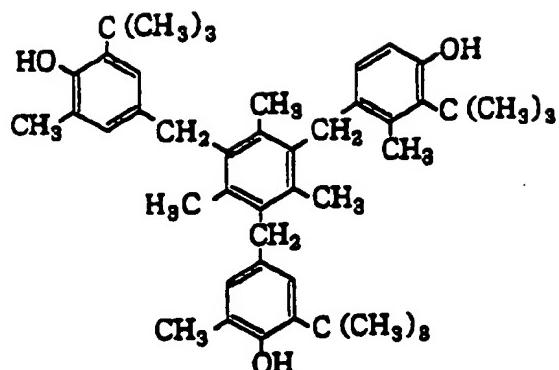
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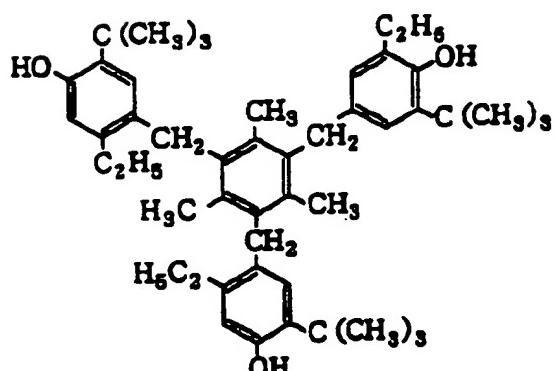
(P - 15)

[0018]

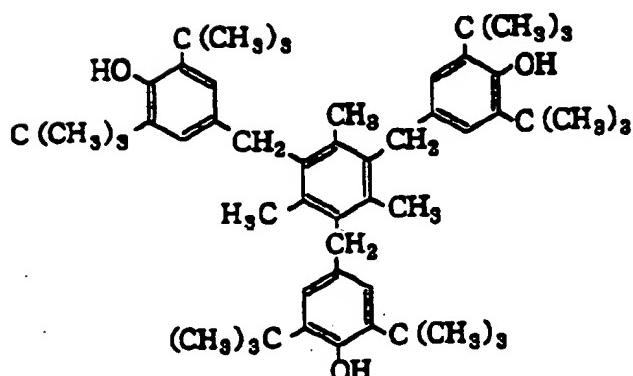
[Formula 9]



(P - 16)



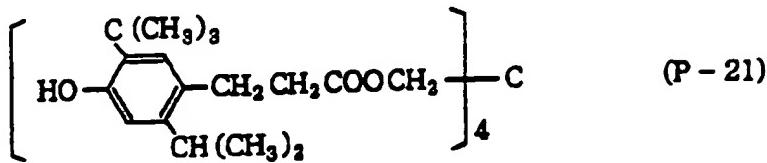
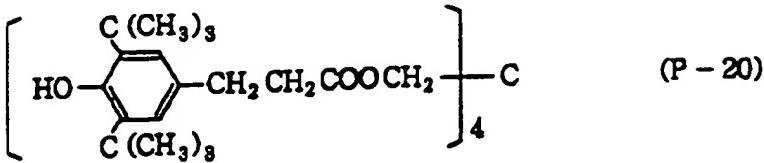
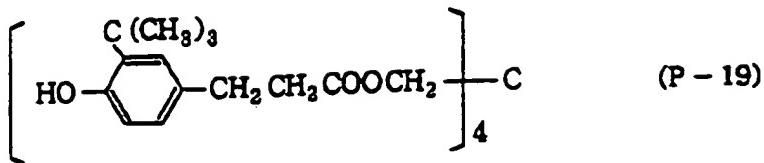
(P - 17)



(P - 18)

[0019]

[Formula 10]

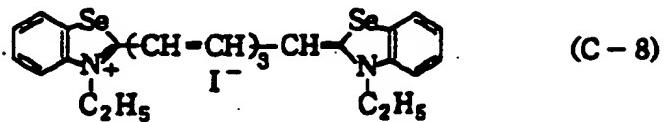
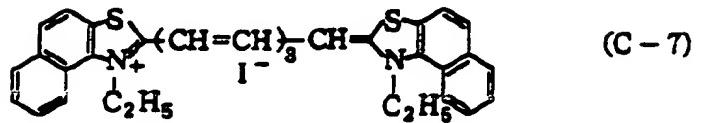
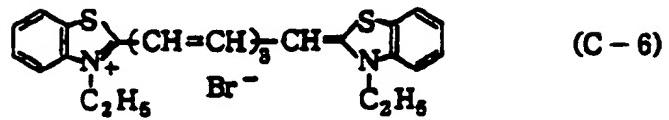
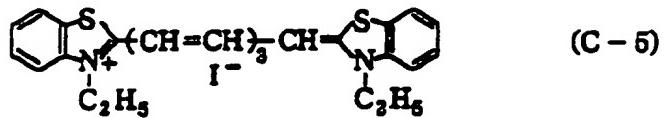
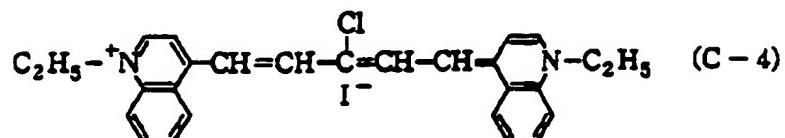
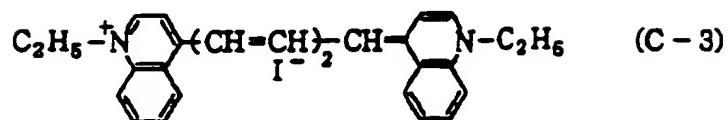
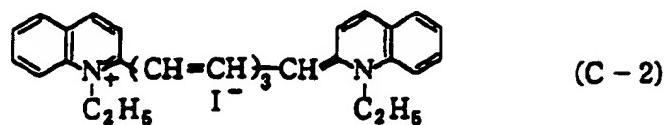
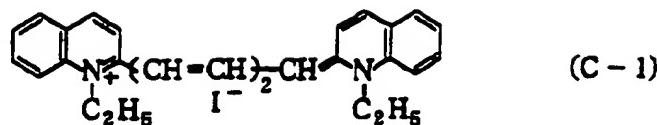


[0020] These photostabilizers for cyanin pigments can be used alone or in combinations of  $\geq 2$  types. They are also not restricted to phenol compounds shown as concrete examples.

[0021] The quantity of photostabilizer employed is ordinarily 0.01-3.0 mol per mol of cyanin pigment. It is also possible to use  $\geq 3$  mol/mol, but in practice it is undesirable because color density is lowered and absorption is lowered. Similarly, when the quantity is small there may be no clear benefit. There are no particular restrictions as to the cyanin pigments which are stabilized, but examples include the compounds indicated below (C-1 to C-21) ([Formula 11] to [Formula 13]).

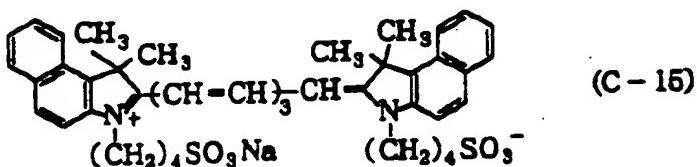
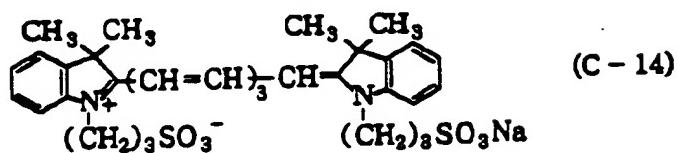
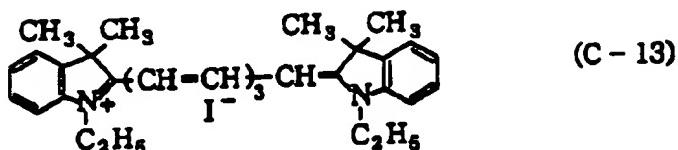
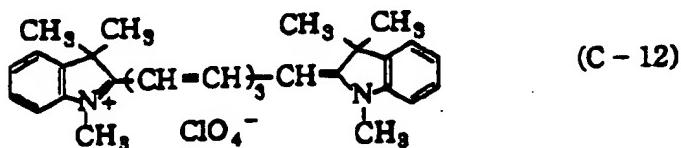
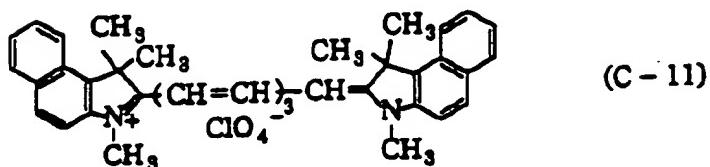
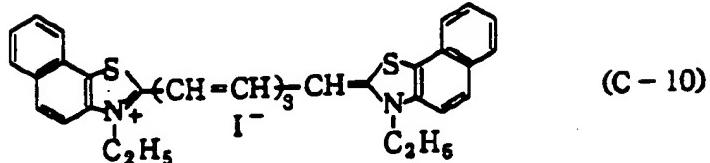
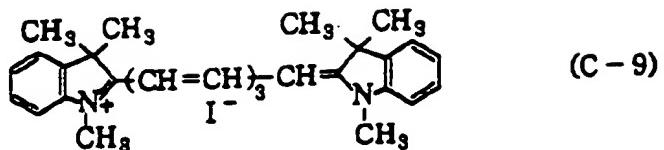
[0022]

[Formula 11]



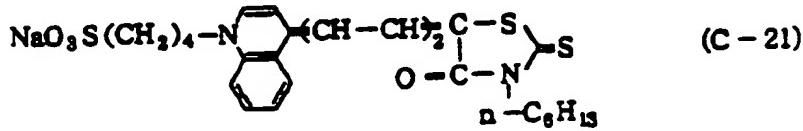
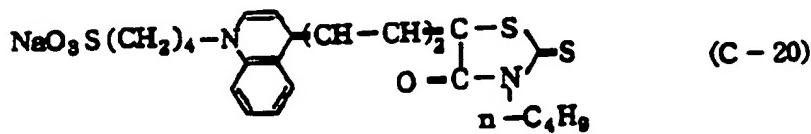
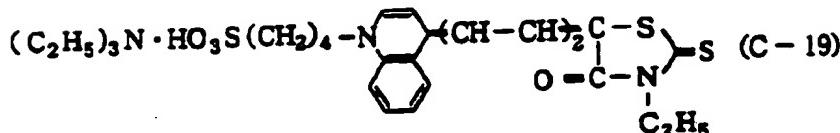
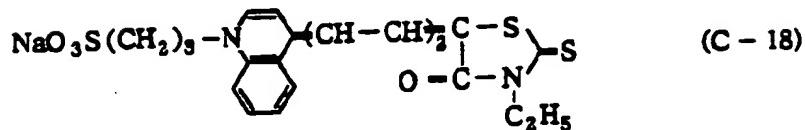
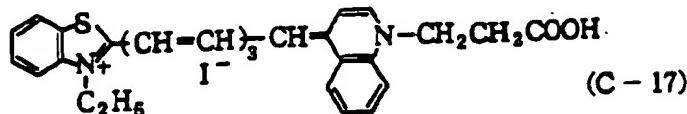
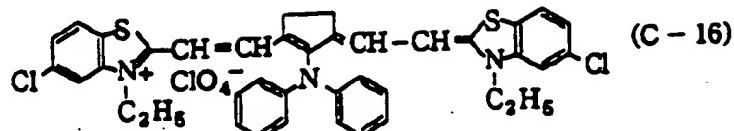
[0023]

[Formula 12]



[0024]

[Formula 13]



[0025] In the present invention, the phenol derivatives can be employed as photostabilizers in thin films of cyan pigments used as recording layers in optical recording media. When these photostabilizers are applied to optical recording media, methods such as dissolving in a solvent together with the pigment and then painting onto the recording medium substrate to form a thin film, etc., can be used.

[0026]

[Embodiments] The present invention is explained in more detail below by means of practical embodiments. In the embodiments the objects which were colored were polycarbonate plates ordinarily used as substrates for recording media; however, similar results are obtained with other substrates such as glass and polymethacrylates, etc.

[0027] Embodiment 1

3 g of a cyanin pigment (C-1) and 2 g of Phenol Compound (A) (P-4) were put into 100 g of ethanol, and after stirring for 1 hour at room temperature the mixture was filtered with a membrane filter (Toyo Filter Paper PTEE, pore size 1.0  $\mu\text{m}$ ) to obtain a pigment solution. This pigment solution was coated onto a polycarbonate plate by a spin coater. The colored polycarbonate plate was exposed inside a light-resistance tester (Irie Seisakusho DR 400T) at a distance of 20 cm. After exposure for 10 hours the percentage fading of the cyanin pigment at 715 nm, the wavelength of peak absorption, was 12.3%, which was a good result.

[0028] Embodiments 2-21

Embodiment 1 was repeated with different combinations of cyanin pigments and bisphenol compounds. The results are shown in Table 1 ([Tables 1-2]): in every case a good result similar to that in Embodiment 1 was obtained.

[0029] Comparison Example 1

When Embodiment 1 was repeated without adding any bisphenol compound, as shown in Table 1 ([Table 2])

there was marked decomposition of the cyanin pigment.

[0030] Comparison Example 2

When Embodiment 1 was repeated using 2,6-t-butyl-4-methylphenol instead of Phenol Compound (P-4), as Table 1 ([Table 2]) shows, there was marked decomposition of the cyanin pigment.

[0031]

[Table 1]

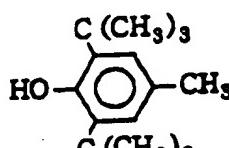
Table 1

Em-body-ment	Photostabilizer	Cyanin pigment	Fade after 10 h (%)
2	P-1	C-2	13.1
3	P-2	C-3	13.0
4	P-3	C-4	13.2
5	P-5	C-5	13.3
6	P-6	C-6	14.0
7	P-7	C-7	12.8
8	P-8	C-8	13.4
9	P-9	C-9	13.2
10	P-10	C-10	13.0
11	P-11	C-11	12.0
12	P-12	C-12	12.8
14	P-14	C-14	12.3
13	P-13	C-13	12.6
15	P-15	C-15	13.5
16	P-16	C-16	13.1

[0032]

[Table 2]

Table 1 (continued)

Em-body-ment	Photostabilizer	Cyanin pigment	Fade after 10 h (%)
17	P-17	C-17	13.4
18	P-18	C-18	12.1
19	P-19	C-19	11.6
20	P-20	C-20	10.5
21	P-21	C-21	11.7
Com-pari-son	Photostabilizer	Cyanin pigment	Fade after 10 h (%)
1	-	C-1	42.0
2		C-1	39.1

[0033]

[Benefits of the invention] The phenol compounds of the present invention are highly safe and easy to handle, and are photostabilizers which have a very excellent photostabilizing effect on cyanin dyes. They are also effective as photostabilizers in optical recorders which have been in high demand in recent years, and enable optical recording media to be offered which have outstanding resistance to light.

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平6-116557

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C 0 9 K 15/08

識別記号

庁内整理番号

F I

技術表示箇所

審査請求 未請求 請求項の数 2(全 14 頁)

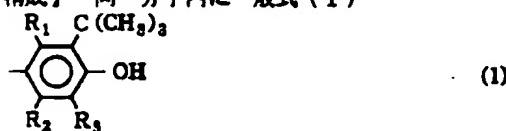
(21)出願番号 特願平4-271475  
(22)出願日 平成4年(1992)10月9日

(71)出願人 000003128  
三井東圧化学株式会社  
東京都千代田区霞が関三丁目2番5号  
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福岡県大牟田市平原町300番地

(54)【発明の名称】 シアニン色素の光安定化剤及び該光安定化剤を含有する光記録媒体

(57)【要約】

【構成】 同一分子内に一般式(1)



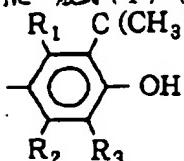
〔式中、R<sub>1</sub>～R<sub>3</sub>は水素原子またはアルキル基を示す。〕で表される構造単位を3個または4個有するフェノール系化合物からなるシアニン色素の光安定化剤及びそれを含有する光記録媒体。

【効果】 取扱いが簡単で安全性が高く、シアニン色素に対する光安定化効果が非常に優れた光安定化剤であり、耐光性に優れた光記録媒体を提供できる。

1

## 【特許請求の範囲】

【請求項1】 同一分子内に一般式(1) (化1)



\* 【化1】

\*

2

(1)

(式中、R<sub>1</sub>～R<sub>3</sub>は水素原子またはアルキル基を示す。)で表される構造単位を3個または4個有するフェノール系化合物からなるシアニン色素の光安定化剤。

【請求項2】 請求項1で示される光安定化剤を含有する光記録媒体。

## 【発明の詳細な説明】

## 【0001】

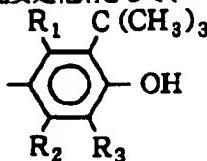
【産業上の利用分野】本発明はシアニン色素の光安定化剤及びそれを含有する光記録媒体に関するものである。

## 【0002】

【従来の技術】光記録媒体いわゆる光ディスクにおいてシアニン色素の薄膜を記録層として用いたものが実用化されている。ここで用いられるシアニン色素は単独では光安定性が悪く、光安定化剤を添加して使用する必要がある。

【0003】光安定化剤としてチオ配位子を有するニッケル化合物などの金属錯体を用いた方法が、特開昭59-219852号、特開昭62-193891号、特開昭62-207688号、特開昭63-19293号、特開昭63-199248号に示されている。この方法は光によって生成する反応性の高い一重項酸素を失活させ、三重項酸素に戻す機構を利用したものであるが、長時間光にさらされるとシアニン色素の分解がかなり進行するという問題点を有する。

【0004】また、他の光安定化剤として、ニトロソ化※



※合物を用いた方法が、特開平2-300287号、特開平2-300288号、特開平2-300289号に示されている。しかし、このニトロソ化合物類は、それ自体毒性が強いか、あるいは光分解物の毒性が強い等の問題を有しているものが多く、ニトロソ化合物を使用する上で人体に対する安全対策が必要である等、好ましくない性質を有している。

【0005】さらに、光安定化剤としてトリニトロフェニルヒドラジル遊離基を有する化合物を用いる方法が、特開平2-304055号に示されている。しかし、トリニトロフェニルヒドラジル遊離基を有する化合物は、爆発性を有しており、取り扱い上、非常に問題である。

## 【0006】

【発明が解決しようとする課題】本発明の目的は、これらの問題点を解決した光安定化剤、すなわちシアニン色素の光安定性を向上させ、取り扱いが簡単で、しかも安全性の高い光安定化剤を提供することである。また、本発明の別の目的は、耐光性に優れた光記録媒体を提供することである。

## 【0007】

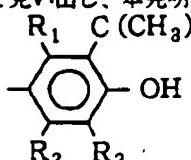
【発明を解決するための手段】本発明者らは、上記課題を解決すべく、鋭意検討した結果、同一分子内に一般式(1) (化2)

## 【0008】

## 【化2】

(1)

【0009】(式中、R<sub>1</sub>～R<sub>3</sub>は水素原子またはアルキル基を示す。)で表される構造単位を3個または4個有するフェノール系化合物が、シアニン色素の光安定性を極めて向上させ、しかも取り扱いが簡単で、かつ安全性の高い性質を有することを見い出し、本発明を完成し ★



40★た。すなわち、本発明は同一分子内に一般式(1) (化3)

## 【0010】

## 【化3】

(1)

3

【0011】〔式中、R<sub>1</sub>～R<sub>3</sub>は水素原子またはアルキル基を示す。〕で表される構造単位を3個または4個有するフェノール系化合物からなるシアニン色素の光安定化剤及び該光安定化剤を含有する光記録媒体である。

【0012】以下、本発明を詳しく述べる。本発明に係わるシアニン色素の一般式(1)（化3）におけるR<sub>1</sub>～R<sub>3</sub>の具体例としては、水素原子、メチル基、エチル基、n-アプロピル基、i-アプロピル基、n-ブチル基、\*

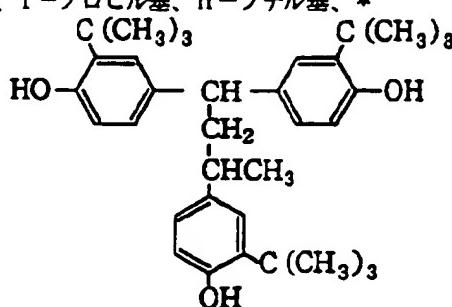
\* i-ブチル基、t-ブチル基、2-メチルブチル基、n-ヘキシル基、n-オクチル基等のアルキル基が挙げられる。

また、一般式(1)（化3）で表される構造単位を3個または4個有するフェノール系化合物の具体例を下記(P-1～P-21)（化4～化10）に示す。

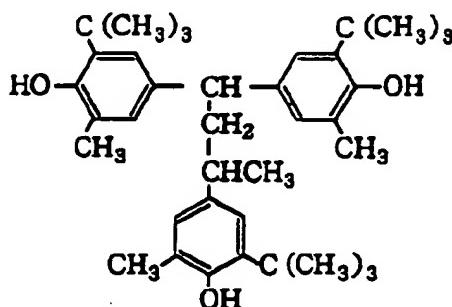
【0013】

【化4】

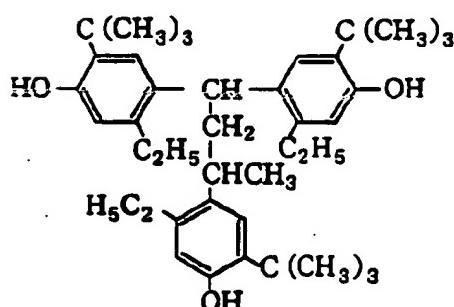
4



(P-1)



(P-2)



(P-3)

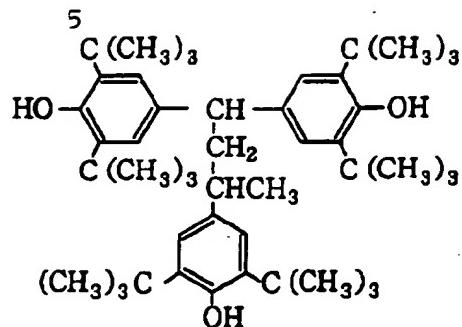
【0014】

※ ※ 【化5】

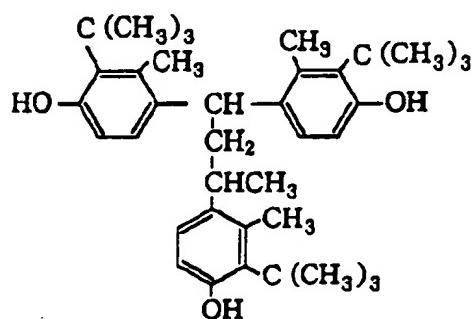
(4)

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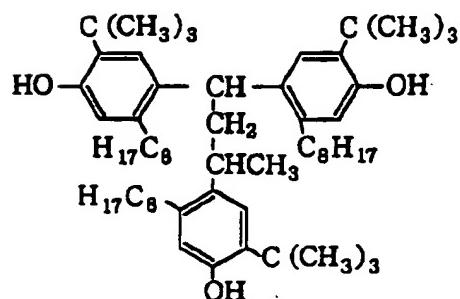
6



(P-4)



(P-5)



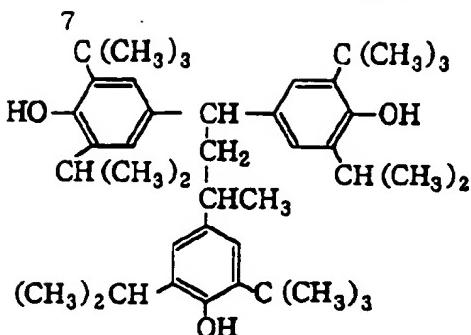
(P-6)

〔0015〕

\* \* 【化6】

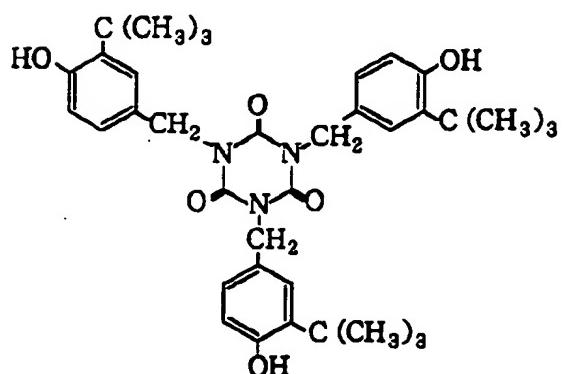
(5)

特開平6-116557

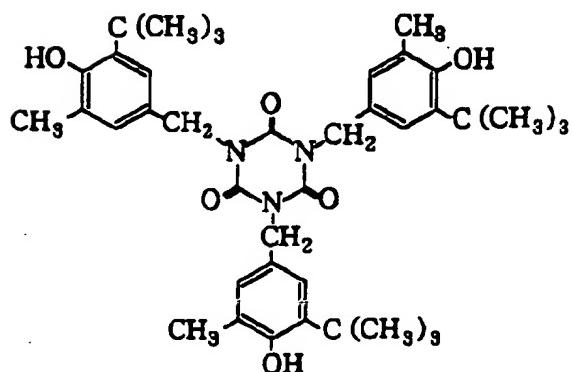


8

(P-7)



(P - 8)

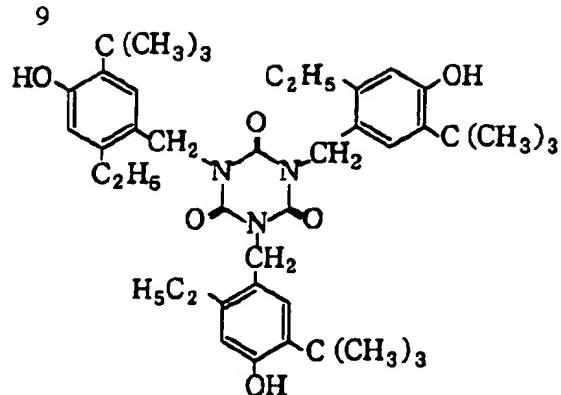


(P - 9)

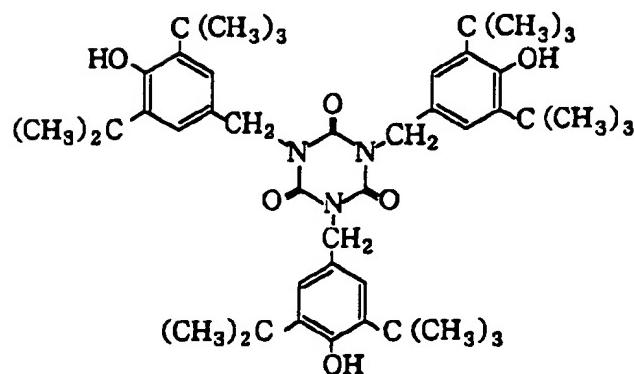
[0016]

\* \* \* (化7)

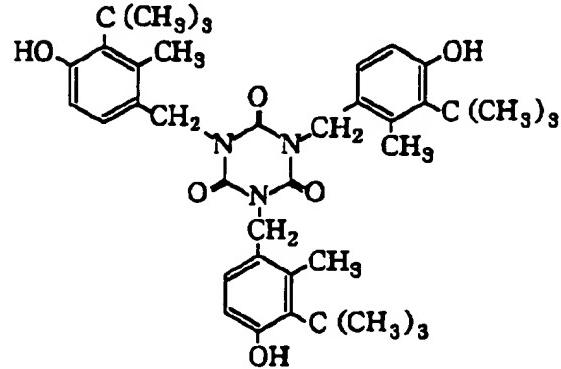
10



(P - 10)



(P - 11)



(P - 12)

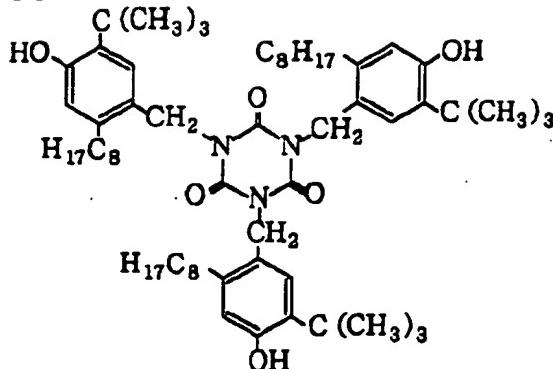
[0017]

\* \* \* (化8)

(7)

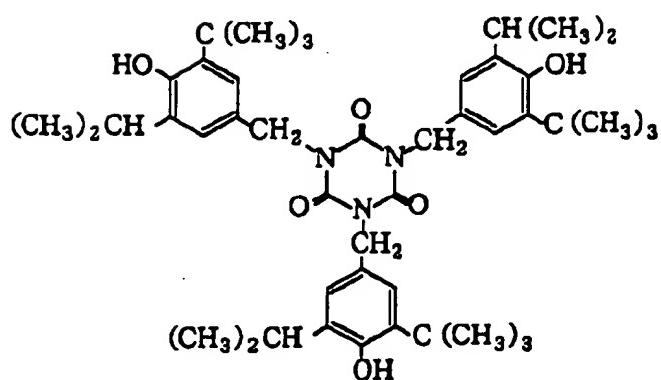
特開平6-116557

11

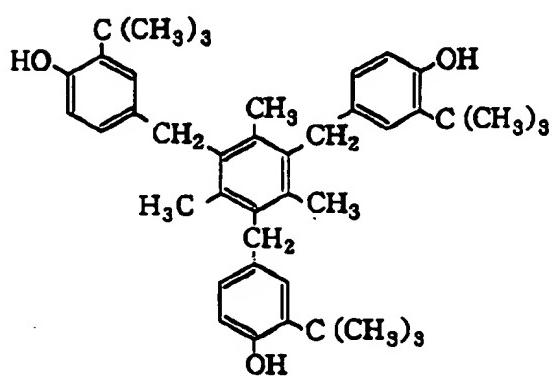


12

(P - 13)



(P - 14)



(P - 15)

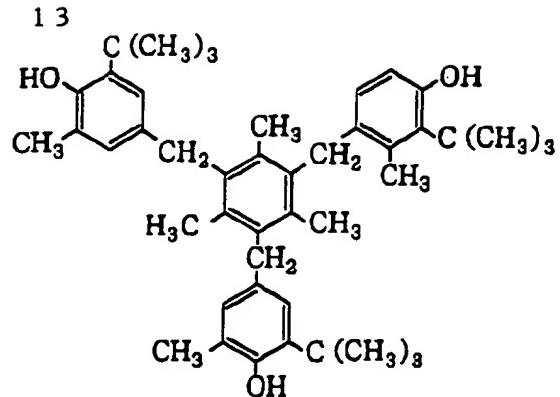
【0018】

\* \* 【化9】

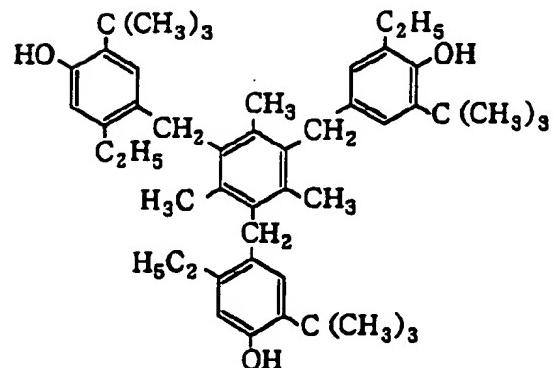
(8)

特開平6-116557

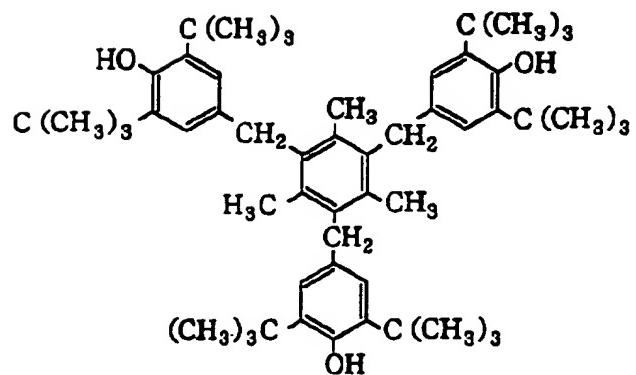
14



(P-16)



(P-17)



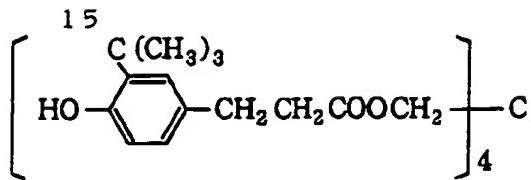
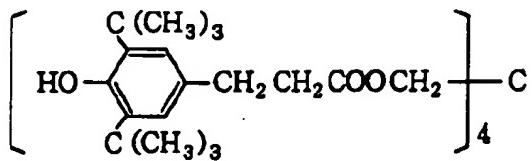
(P-18)

【0019】

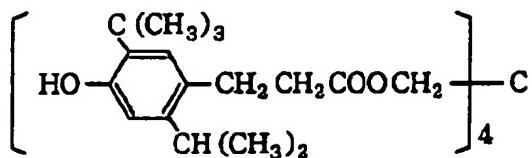
\* \* 【化10】

(9)

特開平6-116557

16  
(P-19)

(P-20)



(P-21)

【0020】これらのシアニン色素の光安定化化合物は、一種類もしくは二種類以上の組み合わせによっても使用できる。また、具体例に示したこれらのフェノール系化合物に限定されるものではない。

【0021】光安定化剤の使用量はシアニン色素に対して、通常、0.01~3.0モル比である。さらに3.0モル比以上を用いてもよいが、シアニン色素の色素濃度が低くなり、吸光度が低くなるため、用途によっては\*

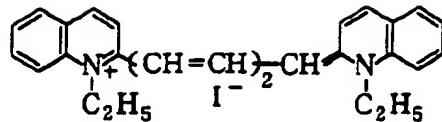
\*不都合を生じる場合がある。また、使用量が少ない場合には効果が明確でないことがある。一方、光安定化の対象となるシアニン色素は、特に限定されるものではないが、具体的には下記(C-1~C-21)(化11~化13)に示される化合物が例示される。

【0022】

【化11】

(10)

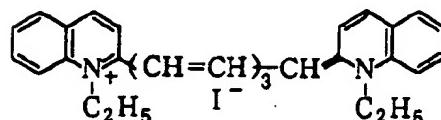
17



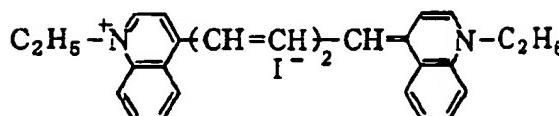
特開平6-116557

18

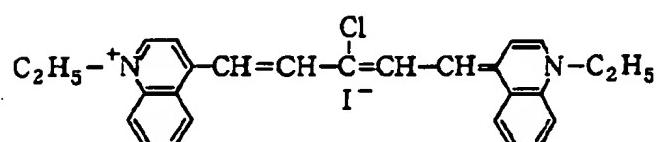
(C-1)



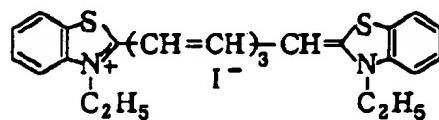
(C-2)



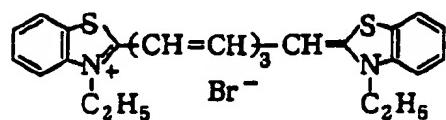
(C-3)



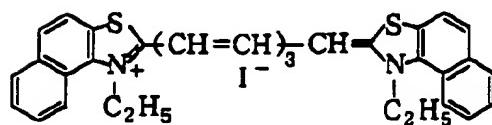
(C-4)



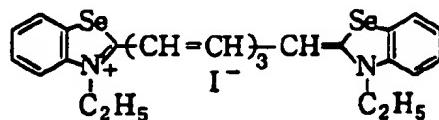
(C-5)



(C-6)



(C-7)



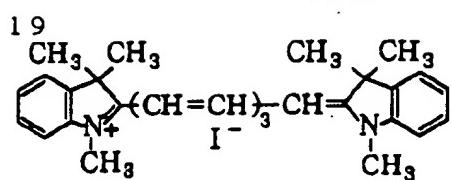
(C-8)

【0023】

\* \* 【化12】

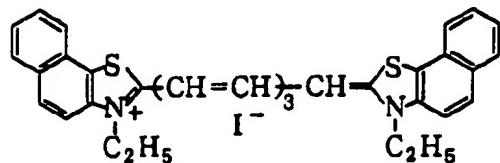
(11)

特開平6-116557

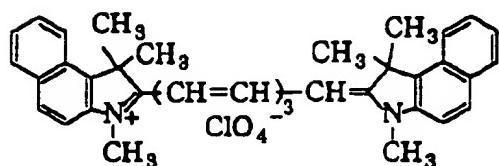


20

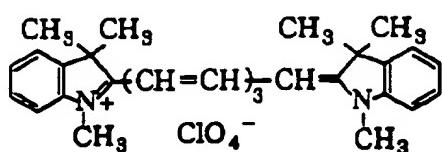
(C-9)



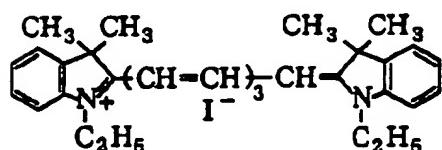
(C-10)



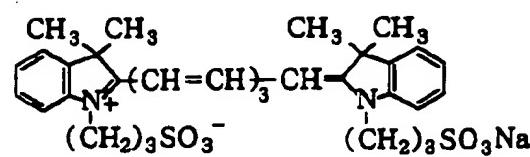
(C-11)



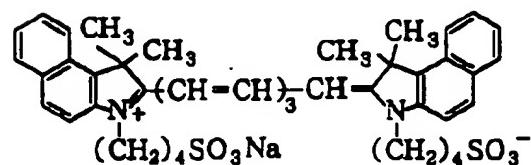
(C-12)



(C-13)



(C-14)



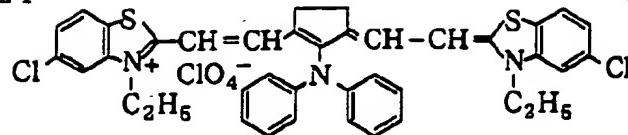
(C-15)

【0024】

\* \* 【化13】

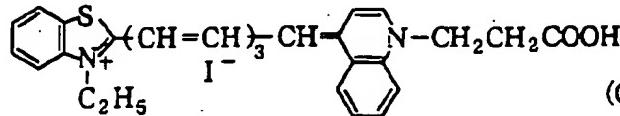
(12)

21

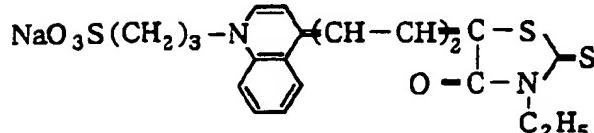


22

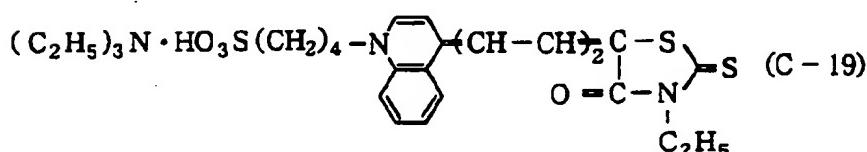
(C-16)



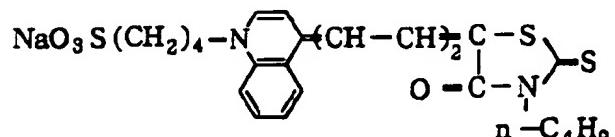
(C-17)



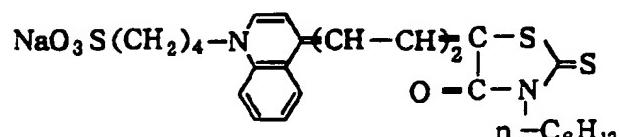
(C-18)



(C-19)



(C-20)



(C-21)

【0025】本発明におけるフェノール誘導体は、シアニン色素の薄膜を記録層として用いる光記録媒体中に光安定化剤として添加使用することができる。これらの光安定化剤を光記録媒体に適用する場合、色素とともに各種溶剤に溶解後、記録媒体の基盤に塗布し薄膜を形成するなどの方法によって行うことができる。

【0026】

【実施例】以下、実施例によって本発明を詳しく説明する。実施例における被着色体としては、通常、光記録媒体の基盤として用いるポリカーボネート板としたが、ガラスやポリメタクリレートなどの他の基盤を用いても同様な結果が得られる。

【0027】実施例1

シアニン色素(C-1)3gおよびフェノール系化合物(P-4)2gをエタノール100g中に入れ1時間室温下で攪拌した後、メンブランフィルター(東洋沪紙製PTEE、孔径1.0μm)を用いて汎過し、色素溶液を得た。本色素溶液をポリカーボネート板基盤上にスピンドル法によって塗布した。この着色ポリカーボネート基盤を耐光試験器(入江製作所製 DR40\*

30\*0T)内で20cmの距離から光照射した。10時間光照射後のシアニン色素の吸収極大波長715nmにおける退色率は12.3%と良好な結果であった。

【0028】実施例2～21

実施例1と全く同様にして、シアニン色素とフェノール系化合物の組み合わせを代えて行った。結果を第1表(表1～2)に示すが、いずれも実施例1同様、良好な結果を得た。

【0029】比較例1

実施例1において、フェノール系化合物を全く添加せずに実施例1と全く同様にして、第1表(表2)に示すようにシアニン色素がかなり分解した。

【0030】比較例2

実施例1において、フェノール系化合物(P-4)の代わりに2,6-ジ-t-ブチル-4-メチルフェノールを用いて実施例1と全く同様にして、第1表(表2)に示すようにシアニン色素がかなり分解した。

【0031】

【表1】

第1表

実施例	光安定化剤	シアニン色素	10時間後の光退色率(%)
2	P-1	C-2	13.1
3	P-2	C-3	13.0
4	P-3	C-4	13.2
5	P-5	C-5	13.3
6	P-6	C-6	14.0
7	P-7	C-7	12.8
8	P-8	C-8	13.4
9	P-9	C-9	13.2
10	P-10	C-10	13.0
11	P-11	C-11	12.0
12	P-12	C-12	12.8
14	P-14	C-14	12.3
13	P-13	C-13	12.6
15	P-15	C-15	13.5
16	P-16	C-16	13.1

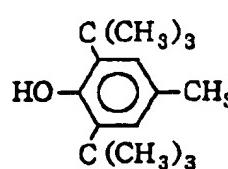
【0032】

\* \* 【表2】

第1表(続き)

実施例	光安定化剤	シアニン色素	10時間後の光退色率(%)
17	P-17	C-17	13.4
18	P-18	C-18	12.1
19	P-19	C-19	11.6
20	P-20	C-20	10.5
21	P-21	C-21	11.7

比較例	光安定化剤	シアニン色素	10時間後の光退色率(%)
1	—	C-1	42.0
2		C-1	39.1

【0033】

【発明の効果】本発明のフェノール系化合物は、取り扱いが簡単で、安全性が高く、しかもシアニン色素に対する光安定化効果が非常に優れた光安定化剤である。ま \*

\*た、近年需要の高い光記録媒体の光安定化剤としても有効であるので、耐光性に優れた光記録媒体を提供することができる。